Corrosion Resistance of Silane-Modified Hydroxyapatite Films on Degradable Magnesium Alloys

Yan-Bin Zhao^{1,2} · Li-Qian Shi^{1,2} · Lan-Yue Cui^{1,2} · Chang-Lei Zhang^{1,2} · Shuo-Qi Li^{1,2} · Rong-Chang Zeng^{1,2} · Fen Zhang^{1,2} · Zhen-Lin Wang³

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Abstract A polymethyltrimethoxysilane (PMTMS)/hydroxyapatite (HA) hybrid coating was successfully fabricated on a magnesium alloy by hydrothermal treatment and immersion method. The microstructure and composition of the coating were characterized by using X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy. The physical properties were investigated using scratch testing. At the same time, the corrosion resistance was evaluated via electrochemical and immersion tests. The results demonstrated that the corrosion resistance of the silane hybrid coating was significantly enhanced compared with the naked magnesium alloy. Especially, the corrosion current density of the PMTMS/HA magnesium alloy was three orders of magnitude lower than that of the bare material.

KEY WORDS: Magnesium alloys; Silane; Hydroxyapatite; Corrosion resistance; Biomaterial

1 Introduction

Owing to their safe degradation, great biocompatibility and excellent mechanical properties, magnesium and its alloys have attracted more and more attention and research in the field of biomaterials [1]. However, low corrosion

resistance, as an inevitable response, poses a limit to the potential applications of magnesium alloys [2].

Surface modification, which is the most popular method on account of its low cost, simplicity and superior performance, is widely employed to improve the corrosion resistance of magnesium alloys, including hydrotalcite coating, chemical conversion coating, micro-arc oxidation (MAO) and plasma electrolytic oxidation (PEO) [3–6]. Especially, the Ca–P coating, such as hydroxyapatite (HA), has been extensively investigated and proved to have the excellent biocompatibility due to its porous microstructure [7]. However, it cannot provide a long-term protection because of the structure. As a result, this coating should be combined with micro-arc oxidation, sol–gel method or hydrothermal treatment, to reduce its in vitro and in vivo corrosion [8, 9].

Among these, we highlight the use of hybrid films formed by the reaction of hydrolysis and condensation of silanes. It has been confirmed that the silane hybrid films are efficient for the protection of metallic substrates against corrosion [10]. Within the common sol–gel processing, the alkoxide precursor with the alkyl group can be hydrolyzed and subsequently condensed via alcohol or water condensation [11]. The

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✉ Shuo-Qi Li
lishuoqi@sdust.edu.cn

✉ Rong-Chang Zeng
rczeng@foxmail.com

¹ College of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China

² State Key Laboratory of Mining Disaster Prevention and Control Co-Founded by Shandong Province and the Ministry of Science and Technology, Shandong University of Science and Technology, Qingdao 266590, China

³ College of Materials Science and Engineering, Chongqing University of Technology, Chongqing 400065, China

advantages of silane films are the low viscosity and the ability to form Si–O–Si bonds, allowing the oligomers to be transported easily and penetrate to a certain depth in order to obtain coatings without cracks [12]. At the same time, the formation of the silane structure can be intended to increase the coating thickness [13]. The resulting hybrid coating can protect metals against corrosion and also provide functional moieties that enable further attachment of bioactive molecules to enhance the interfacial interaction of metal implants with surrounding cells and tissue [14]. However, there are few studies on applying silanes to HA coating for magnesium alloys.

The objective of this work is to deposit the silane-HA hybrid coating on Mg alloys by cross-linking method and hydrothermal treatment [15, 16]. This study could provide a valuable insight for predicting the HA-coated Mg alloy in vivo behavior.

2 Experimental

2.1 Materials and Samples Pretreatment

The substrates used in our experiment were as-extruded AZ31 magnesium alloys with nominal chemical composition (wt%): Al 2.5–3.0, Zn 0.7–1.3, Mn > 0.20, balance Mg, supplied by Beijing Guangling Jinghua Science & Technology Co., Ltd. These substrates were cut into squares with dimensions of 20 mm × 20 mm × 5 mm, ground with 150/400/800/1500 grit SiC sandpapers, washed with a solution of deionized (DI) water and alcohol and dried by warm air. KH_2PO_4 ($M_w = 228.22$, ≥99%), EDTA-Ca ($M_w = 374.27$, 97%) and MTMS ($M_w = 136.22$, 99%) were purchased from Qingdao Jingke Chemical Reagent Co., Ltd.

2.2 Preparation of the Polymethyltrimethoxysilane (PMTMS)/Hydroxyapatite (HA) Coating

The preparation process is schematically illustrated in Fig. 1. The HA coating was prepared via hydrothermal treatment [17]. EDTA-Ca and KH_2PO_4 with a Ca/P molar ratio of 1.67:1 were dissolved into the DI water to obtain solution A. Solution B was prepared by normally stirring and adjusting the pH value for 8.9 with 1 mol/L NaOH solution. Then, this solution was transferred into a Teflon-lined autoclave to immerse the pretreated magnesium alloys. Afterward, the autoclave was heated at 363 K for 360 min. The as-prepared samples were rinsed with DI water and dried with warm air. The HA coating was obtained through the above steps. Then, the alloy samples were dipped into the MTMS solution ($V_{\text{MTMS}}/V_{\text{ethanol}}/V_{\text{DI water}} = 3:10:20$) at 50 °C for 2 h. After aging at 393 K for 2 h, the PMTMS/HA coating was constructed.

2.3 Surface Characterization

The surface and cross-section morphologies of the samples were identified via field-emission scanning electron microscopy (FE-SEM, Nova Nano SEM 450, USA) equipped with energy-dispersive X-ray spectroscopy (EDS) [18]. The phase composition of the samples was analyzed with X-ray diffraction (XRD, Rigaku D/MAX 2500 PC, Japan), with a Cu target at a scanning rate of 8°/min [19]. The diffraction patterns were obtained between 10° and 80°. The possible chemical bonding formed in the samples was confirmed via Fourier transform infrared spectroscopy (FTIR, Nicolet 380, Thermo electron, USA) [20].

2.4 Corrosion Tests

The corrosion resistance of the samples was evaluated by potentiodynamic polarization curves and electrochemical impedance spectra (EIS), which were obtained via an electrochemical analyzer (PAR Model 2273, Princeton, USA) [21]. The cell setup was a three-electrode system in which the samples were used as the working electrode, while a saturated calomel electrode and a platinum sheet were used as the reference and the counter electrodes, respectively. The polarization curves started from −2 to −1 V at a scan rate of 1 mV/s. The EIS studies were carried out at open-circuit potential for 10 mV sinusoidal amplitude over a frequency range from 100 kHz to 10^{-2} Hz. These experiments were performed in Hank's balanced salt solution (HBSS): 8.0 g/L NaCl, 0.4 g/L KCl, 0.14 g/L CaCl_2 , 0.1 g/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.35 g/L NaHCO_3 , 1.0 g/L $\text{C}_6\text{H}_6\text{O}_6$ (glucose), 0.06 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.06 g/L KH_2PO_4 and 0.06 g/L $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

Usually, polarization resistance (R_p), which is inversely proportional to the corrosion rate, can be calculated using the simplified Stern–Geary equation: $R_p = (b_a b_c) / [2.303 I_{\text{corr}} (b_a + b_c)]$, where b_a and b_c represent the Tafel slopes of the anode and cathode, respectively, while I_{corr} is the corrosion current density.

The hydrogen evolution setup design was investigated by placing the samples under an inverted funnel in HBSS at 37.5 ± 0.1 °C, which was connected to a graduated burette. The water level in the burette was intermittently recorded during the immersion for 150 h with full surface exposure. Finally, the samples were taken out and dried by warm air for further characterization after the experiment.

2.5 Scratch Testing

The bonding force between the coating and the matrix could be characterized by MML Nanotest system (Micro Materials, Ltd.) with Rockwell diamond probe (its tip diameter was 25 μm). The nanoscratch tests were carried

Fig. 1 Schematic representation of the preparation of PMTMS/HA coating

out with the scan velocity of 2 mm/min by linearly increasing the load to 10 N, until the total scratch length reached 2 mm. The tests were repeated for three times. The scratch images were captured by using an in situ optical microscope system in order to locate initial failure of the coating.

3 Results

3.1 Composition and Surface Characterization of the Films

The XRD spectra of AZ31, HA and PMTMS/HA films are shown in Fig. 2. Peaks corresponding to $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ appeared in the spectra of both PMTMS/HA/AZ31 and HA/AZ31 [22–24]. For the PMTMS/HA coating, a weak diffraction peak of silane was detected at 22° , which demonstrated that the hybrid coating was prepared successfully [25, 26]. Thus, the XRD analysis provided clear evidence that the hydroxyapatite coating and the silane film were successfully prepared onto the surface of the magnesium alloys.

The FTIR spectra provide a qualitative analysis about organic groups in the coating as shown in Fig. 3. Firstly, the spectrum of HA/AZ31 in Fig. 3a presented an absorption peak of $\text{O}-\text{H}^-$ at 3470 cm^{-1} [27]. The intense

Fig. 2 XRD patterns of the AZ31 substrate *a*, the HA *b* and the PMTMS/HA *c* films

band at 1041 cm^{-1} showed the stretching modes of PO_4^{3-} , while the bands at 608 and 563 cm^{-1} were both the bending modes of PO_4^{3-} . Moreover, the adsorption bands at 876 and 1450 cm^{-1} are both due to the CO_3^{2-} groups. A reliable explanation for these peaks is that small portions of the PO_4^{3-} groups were substituted by the CO_3^{2-} [28]. Secondly, in Fig. 3b, the spectrum of the PMTMS/HA/AZ31, which presented absorption peaks at 1268 and 775 cm^{-1} , corresponds to the Si-C groups, while the presence of C-H stretching vibrations was supported by the peaks at 2980 cm^{-1} [29]. The absorption peaks at

Fig. 3 FTIR patterns of the HA *a* and the PMTMS/HA *b* films

1120 cm^{-1} were attributed to an asymmetric Si–O–C stretching band, and the peak at 1030 cm^{-1} was assigned to the Si–O–Si [30]. Therefore, the FTIR spectra clearly indicated that the PMTMS/HA coating was successfully synthesized with silane and hydroxyapatite.

Figure 4 illustrates the SEM morphology and the corresponding EDS spectra of HA and PMTMS/HA films. For the HA coating, it was found that the plate-shaped grains were accumulated on the surface of magnesium alloys and some grains were stacked to form the flower-like structure. The EDS spectrum of point A shows that the corrosion products are mainly composed of Ca (11.76%), P (9.42%), O and C. Compared with the SEM morphology of the HA film, the PMTMS/HA coating was more smooth, uniform and dense, except for some clusters due to the self-condensation of silane. The EDS analysis showed that the

approximate chemical composition of the composite coating was C (29.88%), O (48.92%) and Si (21.20%). Consequently, the silane hybrid coating could well cover the bare magnesium alloy, providing an effective and long-term barrier.

The cross-sectional microstructure and the elemental mapping results are shown in Fig. 5. The thickness of the PMTMS/HA coating was approximately 2.7 μm , while the distribution of Ca, P, Si and O in the hybrid film was unified, uniform and denser. The results also indicated that the silane completely filled the porous structure of the hydroxyapatite.

3.2 Electrochemical Corrosion Test

The potentiodynamic polarization curves (Tafel) are applied to investigate the anti-corrosion properties of samples in Fig. 6, and the corresponding results calculated by extrapolation based on the polarization plots are summarized in Table 1. The I_{corr} values for bare AZ31, HA coating and PMTMS/HA coating were equal to 1.84×10^{-5} , 1.77×10^{-6} and $3.86 \times 10^{-8} \text{ A/cm}^2$, respectively. The I_{corr} value of the silane hybrid HA film was approximately 2.18% of that of the HA film and 0.21% of that of the AZ31. The list of the values of R_p in the descending order is: PMTMS/HA coating ($3.87 \times 10^6 \Omega \text{ cm}^2$) > HA coating ($3.94 \times 10^4 \Omega \text{ cm}^2$) > the AZ31 substrate ($3.76 \times 10^3 \Omega \text{ cm}^2$). Thus, the silane hybrid coating exhibited clearly an excellent corrosion protection for the AZ31 magnesium alloy.

EIS was involved to investigate the corrosion behavior of samples, and the corresponding results are shown in Fig. 7a–c. Firstly, the diameters (two capacitive loops) of

Fig. 4 Surface morphologies and the corresponding EDS spectra of the HA *a*, *b*, *c* and the PMTMS/HA films *d*, *e*, *f*

Fig. 5 Cross-sectional morphology **a** and the elemental mapping results **b**, **c**, **d**, **e** of PMTMS/HA film

Fig. 6 Polarization curves of the AZ31 **a**, the HA coating **b** and the PMTMS/HA coating **c**

the PMTMS/HA/AZ31 are the largest among the three samples in Fig. 7a. Secondly, the silane hybrid HA film had the highest value of $|Z|$. Thirdly, in Fig. 7c, the phase angle of curve iii is loftier and wider, revealing that the hybrid film was uniform and denser. Therefore, these evidences indicate that the PMTMS/HA coating superiorly enhanced the corrosion resistance of the magnesium alloy.

In order to better understand the mechanism of the corrosion behavior in HBSS, the equivalent electrical circuit (EEC) for EIS plots was applied to fit the experimental data via ZSimpWin software. Figure 7d–f shows the EECs

of the AZ31 substrate, the HA film and the PMTMS/HA film, respectively. In these equivalent circuits, R_s was the solution resistance between the reference electrode and the working electrode, R_{ct} denoted the charge transfer resistance, and R_c represented the coating resistance (virtual pore resistance) paralleled with a constant phase element (CPE, $Y_{CPE}(\omega) = 1/Z_{CPE} = Q_a(j\omega)^n$). Based on the proposed equivalent circuit models and the properties of the composite coating, the EIS curves were best fitted and the corresponding values of the equivalent circuit parameters are listed in Table 2. As it is well known, higher R_{ct} values represent lower dissolution rates [31]. The low R_{ct} value of the AZ31 substrate ($855 \Omega \text{ cm}^2$) suggests a high corrosion rate. Conversely, the increased R_{ct} value of the HA/AZ31 ($2826 \Omega \text{ cm}^2$) emphasizes the beneficial effect of the hydroxyapatite film. Moreover, the large R_{ct} value of the PMTMS/HA film ($7108 \Omega \text{ cm}^2$) demonstrates that the composite coating clearly enhances the corrosion resistance of the magnesium alloy.

3.3 Immersion Tests

The corrosion rate during immersion can be determined via hydrogen monitoring, which is performed by the drainage gas collecting method [32]. The hydrogen evolution rates (HERs) of AZ31 substrate, HA coating and PMTMS/HA coating in HBSS are shown in Fig. 8. The HERs of the tested samples could be ranked in the increasing order as

Table 1 Electrochemical parameters of the polarization curves in HBSS

Sample	E_{corr} (V/SCE)	I_{corr} (A/cm^2)	B_a (mV/decade)	$-b_c$ (mV/decade)	R_p ($\Omega \text{ cm}^2$)
AZ31	−1.47	1.84×10^{-5}	94.31	231.54	3.76×10^3
HA/AZ31	−1.39	1.77×10^{-6}	92.62	218.65	3.94×10^4
PMTMS/HA/AZ31	−1.45	3.86×10^{-8}	146.83	256.32	3.87×10^6

Fig. 7 **a** Nyquist plots and fitting curves, **b** Bode plots and **c** Bode plots of the phase angle versus frequency for bare AZ31 substrate *i*, HA/Mg film *ii* and PMTMS/HA film *iii*, and the corresponding equivalent electric circuits for EIS: **d** AZ31 substrate, **e** HA/Mg film, **f** PMTMS/HA film in HBSS

Table 2 Fitted electrochemical parameters of EIS after various immersion periods

Sample	R_s (Ω cm ²)	Q_1 (Ω^{-1} s ^{<i>n</i>} /cm ²)	N_1	R_{ct1} (Ω cm ²)	Q_2 (Ω^{-1} s ^{<i>n</i>} /cm ²)	R_{ct} (Ω cm ²)	C (F/cm ²)	R_L (Ω cm ²)	L (H cm ²)
AZ31	67.82	1.457×10^{-5}	0.86	—	—	852	—	653.4	647.3
HA	64.86	1.264×10^{-5}	0.88	—	9.32×10^{-4}	2826	—	1367	3.279×10^4
PMTMS/HA	42.95	1.183×10^{-7}	0.78	271.82	2.05×10^{-6}	7108	1.42×10^{-7}	9.56×10^5	8.552×10^6

follows: the PMTMS/HA coating < the HA coating < the AZ31 substrate. Thus, the silane hybrid HA coating possessed the best corrosion resistance in HBSS, which was in accordance with the electrochemical corrosion tests.

Figure 9 illustrates the SEM morphology and the corresponding EDS spectra of the samples immersed in the HBSS for 150 h. First of all, some cracks could be observed on the surface of the bare AZ31 owing to the corrosion of HBSS in Fig. 9a. Secondly, for the HA film (Fig. 9b), many corrosion products had accumulated on the surface, which may be regarded as a protective barrier for the substrate. Thirdly, the PMTMS/HA film (Fig. 9c) exhibited a well-preserved surface characteristic, except for a few localized globules, which were on account of the self-polycondensation of silane [33]. The presence of the peaks of Mg, C, O, P and Ca in the EDS spectra (Fig. 9d, e) clearly confirmed the presence of corrosion products, such as Mg(OH)₂ and Ca–P precipitates. At the same time, Fig. 9f also indicates that no severe attack occurred on the PMTMS/HA film after immersion through the contents of O (46.31%), Si (24.30%) and C.

Fig. 8 HERs results of the bare AZ31 *a*, the HA film *b* and the PMTMS/HA film *c* in HBSS for 150 h

The XRD spectra of AZ31, HA/AZ31 and PMTMS/HA/AZ31 are shown in Fig. 10. Peaks corresponding to the hydroxyapatite appeared in the spectra of both HA and PMTMS/HA films, indicating that the HA coating could not be seriously corroded by the HBSS. Furthermore, also a

Fig. 9 Surface morphologies and the corresponding EDS spectra of the AZ31 **a, d**, the HA/Mg **b, e** and the PMTMS/HA/AZ31 **c, f** immersed in HBSS for 150 h

diffraction peak of silane was detected at 22° for the PMTMS/HA coating. Thus, these results indicate that the silane-modified hydroxyapatite film was relatively complete after immersion.

3.4 Nanoscratch Testing

The adhesion strength or the bonding force between the coating and the substrate was investigated via the nanoscratch tests, which could be used to measure the critical load (L) during the adhesive failure of the coating/substrate system [34]. Figure 11 indicates the relationships between the load and the sliding distance. The critical load of the PMTMS/HA coating was 3328 mN, indicating that about 3.3 N (load) is needed to destroy this silane hybrid coating. At the same time, the L_{HA} was 2492 mN, which showed an

excellent adhesion of the HA coating with the AZ31 magnesium alloy. Thus, the results demonstrated that the silane could further enhance the adhesion strength in the PMTMS/HA-coated AZ31.

4 Discussion

4.1 Formation of the Silane Hybrid Coating

According to the elemental compositions of Ca, P, C and O in the EDS analysis (Fig. 4c) and the presence of PO_4^{3-} and OH^- groups in the FTIR patterns (Fig. 3a), the

Fig. 10 XRD patterns of the AZ31 **a**, the HA/AZ31 **b** and the PMTMS/HA/AZ31 **c** immersed in HBSS for 150 h

Fig. 11 Nanoscratch test results of the HA and the PMTMS/HA coating

formation of the hydroxyapatite coating could be clearly confirmed. During the hydrothermal treatment, the OH^- firstly reacted with the dihydrogen phosphate (H_2PO_4^-), thereby yielding the hydrogen phosphate (HPO_4^{2-}). Then, the HPO_4^{2-} would combine with Ca^{2+} to form the CaHPO_4 . This reaction sequence is represented in reactions (1) and (2):

At the same time, the HPO_4^{2-} could also react with OH^- to generate the phosphate (PO_4^{3-}), which would then react with the Ca^{2+} to form the $\text{Ca}_3(\text{PO}_4)_2$ according to reactions (3) and (4):

It is noted that peaks of CaHPO_4 and $\text{Ca}_3(\text{PO}_4)_2$ were both absent from the XRD patterns. Thus, probably the HPO_4^{2-} and the PO_4^{3-} were transformed into hydroxyapatite as shown in reactions (5) and (6):

Similarly, the formation of the silane-HA hybrid coating was clearly demonstrated through the content of Si, O and C in the EDS (Fig. 4f) as well as by the appearance of the Si–C groups, the Si–O–C band, the Si–O–Si chain and the Si–OH band in the FTIR patterns (Fig. 3b). The PMTMS was prepared by methyltrimethoxysilane (MTMS) as follows:

Then, the $\text{CH}_3\text{--Si--}(\text{OH})_3$ would cross-link the $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ by hydrolysis condensation reactions to form the Si–O–Si groups.

4.2 Corrosion Mechanism

The corrosion mechanism of the PMTMS/HA coating could be confirmed via the HER test, plus the SEM, the EDS and the XRD analyses. Firstly, the silane completely covered the surface of the HA coating, which effectively blocked the penetration of HBSS. Then, the silane underwent a self-polycondensation because of the swelling of the PMTMS, forming many globules. Secondly, with the expansion of the silane, the hydroxyapatite film was exposed to the HBSS in some areas, which may be considered as a barrier for the substrate. Finally, the HA film

was destroyed, and then, the newly unprotected AZ31 was corroded by the HBSS following reactions (8), (9) and (10):

5 Conclusions

1. A silane hybrid HA coating was successfully fabricated via hydrothermal treatment and silane cross-linking method with the enhanced anti-corrosion performance.
2. The electrochemical tests demonstrated that the PMTMS/HA film had the lowest I_{corr} ($3.86 \times 10^{-8} \text{ A/cm}^2$) of all the samples.
3. The PMTMS/HA coating had the lowest H_2 evolution rate during the immersion tests.
4. Owing to the physical and chemical stabilities, the combination of HA and silane resulted in a significant improvement in the corrosion resistance of magnesium alloys.

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